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THE MECHANISM OF OXIDE FORMATION IN  
THE INITIAL STAGES OF OXIDATION

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## THE MECHANISM OF OXIDE FORMATION IN THE INITIAL STAGES OF OXIDATION

This quarter's work consisted primarily of further experimental studies of the reaction of oxygen on tungsten at temperatures between room temperature and  $1000^{\circ}\text{C}$  with oxygen pressure between  $10^{-8}$  and  $10^{-4}$  mm Hg. From this work has evolved a general description of the oxidation process on tungsten in terms of the more influential parameters of substrate temperature, crystallography, and oxygen pressure.

Before discussing the experimental results, a few comments on the important matter of differentiation between adsorption and the formation of a crystalline second phase are in order. From the rather definitive studies of the adsorption of oxygen on tungsten,<sup>1</sup> it may be concluded that two layers may be chemisorbed, one stable to  $\sim 300^{\circ}\text{C}$ , the other stable to  $\sim 1000^{\circ}\text{C}$ . Additional oxygen may be accommodated in a weakly-bound physisorbed state at low temperatures. While the work function anisotropy of the field-emitter surface with respect to crystallography is not constant as a function of coverage and the surface density of adsorbate varies with crystallography, the availability of a multitude of almost equally favorable sites for chemisorption gives rise to rather uniform electron emission from a given crystallographic region during the process of chemisorption from the gas phase. Since the topography changes gradually from one region to another, emission intensity changes more or less continuously as a function of crystallography and of time during the process of adsorption. That the chemisorption process is revealed in this manner, is the result of the resolution limit of the microscope, i.e., highly localized changes cannot be resolved. Physisorption, however, may give rise to resolvable slight variations in local emission intensity due to the possible existence of highly preferred sites and a small field enhancement effect.

On the other hand, the transformation to a second crystalline phase on a localized scale is expected to give rise to a sharp discontinuity in electronic properties. This discontinuity will be observed as soon as the size of the transformed region exceeds the resolution limit of the microscope ( $\sim 20 \text{ \AA}$ ). Furthermore, if the second phase protrudes above the surface of the surrounding region, the discontinuity will be intensified by the field enhancement effect. This is to say, then, that emission discontinuity on a highly localized scale accompanies the nucleation of a crystalline second phase.

The reaction of oxygen at pressures between  $10^{-8}$  and  $10^{-4}$  mm Hg on the tungsten substrate at temperatures under  $500^{\circ}\text{C}$  is characterized at constant temperature and pressure by an apparent end-point in the

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<sup>1</sup>For a fairly recent review of this work see DMIC Report No. 155, 1961, Oxidation of Tungsten by Barth and Rengstorff, pp. 23-35.

reaction sequence of emission patterns. The end-point depends upon both temperature and pressure. For example, let  $T_1 < T_2$ ,  $P_1 < P_2$ , and A, B, C, and D represent successive emission patterns corresponding to the reaction (with T being the temperature and P the pressure). Then, at  $T_1$  and  $P_1$ , the reaction might be characterized by  $A \rightarrow B \rightarrow C$ , with C the end-point, while at  $T_1$  and  $P_2$ , the reaction would be  $A \rightarrow B \rightarrow C \rightarrow D$ . The effect of increased temperature at constant pressure would be opposite that given above, i.e., if D is the end-point for  $T_1$ , C might be the end-point for  $T_2$ . In addition, the length of time required to reach a given stage in the reaction increases as substrate temperature is increased at constant pressure. This indicates, of course, a greater rate of desorption from the surface and a greater rate of diffusion into the bulk tungsten. Emission discontinuities on a highly localized scale are not apparent in the emission patterns corresponding to these reactions.

At higher substrate temperatures, and pressures under  $10^{-6}$  mm Hg, the reaction sequence of emission patterns is again characterized by gradual changes in emission intensity and end-points (through these are not the same as those encountered at lower substrate temperatures). With increased oxygen pressures, the isothermal-isobaric reactions by-pass the end-points characteristic of the reactions at lower pressures and eventually give rise to highly localized emission discontinuities in particular crystallographic regions. The discontinuities define relatively small areas of high emission intensity which are interpreted as oxide nuclei or microcrystallites. In the crystallographic regions in which the nuclei first appear, the nuclei are relatively closely packed with the distance between adjacent nucleating centers of the order of 100 Å, and appear more or less simultaneously in a particular crystallographic region. The specific crystallographic regions involved depend upon the substrate temperature and pressure. The data of Table I demonstrate this dependence for substrate temperatures of 750 and 1000 C. Oxygen pressures are given in terms of ionization gauge measurements. The crystallographic regions refer to large segments of the surface such as would result if the entire surface area of the emitter was divided into {110}, {111}, {211}, and {100} regions. The absence of a crystallographic region in which nuclei "appear later" does not necessarily mean that nuclei would not appear if the experiment had been of longer duration.

TABLE I

Substrate Temperature (°C)	Oxygen Pressure (mm Hg)	Crystallographic Region in which Nuclei	
		appear first	appear later
750	$10^{-6}$	{111} and {211}	
750	$10^{-6}$	{111} and {211}	{110}
1000	$10^{-6}$	{111} and {100}	

The growth characteristics of the nuclei which have been observed in the {110} region are somewhat difficult to interpret. In the first place, these nuclei do not occur simultaneously, but increase in number with time. The emission from a given nuclei may disappear, then reappear in the pattern with increasing reaction time. Impingement of nuclei may not be apparent, and increased field enhancement for a particular nuclei is frequently observed as a function of time. Such phenomena have been observed with oxide nuclei on tantalum as well. While such behavior may be rationalized as preferential growth away from the surface, further experimental evidence seems necessary.

In conclusion, the oxygen-tungsten reaction at oxygen pressures to  $10^{-5}$  mm Hg and substrate temperatures between 30° and 500°C is characterized by a stable adsorbed state with no noticeable tendency for oxide formation. At temperatures between 500° and 1000°C, adsorption occurs initially and is followed by the nucleation of oxide at highly preferred sites on the substrate if oxygen pressures exceed  $10^{-5}$  mm Hg. The location of nucleation sites with respect to crystallography is dependent upon substrate temperature and oxygen pressure.

Work in the immediate future will attempt to (1) define with more precision the limiting temperatures and pressures for the various characteristics of the reactions on tungsten and tantalum; (2) improve the control of oxygen pressure, and (3) generally extend the current studies.

Papers Published During This Period:

A manuscript has been prepared which will be published as part of the proceedings of the Symposium on Oxidation of Refractory Metals held in New York City on October 30, 1962 as part of the Fall meeting of the Metallurgical Society of A.I.M.E.

Degrees Granted: None

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